# Dynamic Mechanical Properties of Polypropylene Films (Special Issue on Polymer Chemistry, II)

AUTHOR(S):

Chu, Hyong-Dong; Kitamaru, Ryozo; Tsuji, Waichiro

# Dynamic Mechanical Properties of Polypropylene Films

Chu Hyong-Dong, Ryozo KITAMARU and Waichiro TSUJI*

(Tsuji Laboratory)

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The dynamic mechanical properties of polypropylene fractions which encompass a wide range in molecular weight and crystallinity have been studied. In a set of experiments for well annealed fractions, it is found that $T_\alpha$ (temperature where the loss angle tangent $\tan\delta$ goes through a maximum value) shifts to a higher temperature and $\tan\delta$ at the temperature decreases as the crystallinity increases. In studying the dynamic mechanical properties of samples quenched from melt to different temperatures, it is found that $T_\alpha$ elevates to a higher temperature and $\tan\delta$ at $T_\alpha$ increases as the quenching temperature is decreased when samples are quenched from the melt. In another set of experiments for drawn samples, it is confirmed that if quenched films from melt are drawn and annealed, $T_\alpha$ shifts generally to a higher temperature and $\tan\delta$ at $T_\alpha$ decreases with the increase of draw ratio. In addition, the dependency of the mechanical properties on the thermal history before and after drawing and on drawing temperature has been studied.

## 1. INTRODUCTION

In general, the relation between the mechanical properties and the fine structure of crystalline polymers is one of the important problems. In order to characterize the physical properties of stereoregular polymer, such molecular factors as the average molecular weight, the distribution of molecular weight, the fraction of stereoregular part and the continuity of the regular part should be at least considered.

When the solid structure of a polymer is being formed, these molecular factors will give effects on the resultant structure but the mechanism will be extremely complicated. For polypropylene Sauer[1], Muns[2], McCrum[3] and Takayanagi[4,5] have studied the viscoelastic properties and also Schooten[6] has studied the static and dynamic mechanical properties of fractionated polypropylene samples. Through these studies it was found that the $\alpha_a$-absorption in the curve of the loss tangent $\tan\delta$ or loss modulus E'' *vs.* temperature ordinarily took place in the vicinity of room temperature. Sauer *et al.* concluded that the absorption was due to the micro-Brownian motion of the main chains in the amorphous phase of the polymer, and the other authors agreed with the conclusion. But there still remain many problems obscured as yet about the relation between the viscoelastic behavior and the fine structure.

The purpose of the present study is to elucidate the relation between $\alpha_a$-absorption in $\tan\delta$-temperature curve and the fine structure of polypropylene

* 朱 炫 敬, 北丸 竜三, 辻 和一郎

film and to interpret the relation in terms of the mobility of chain segments of the molecules in the amorphous phase. The tan $\delta$-temperature curves were obtained in the temperature range from $-50°$ to 100°C for the whole polymer of polypropylene having different thermal histories and its fractions, using a vibrating reed method[7]. In addition, the viscoelastic properties of drawn polypropylene films were studied as a function of draw temperature, draw ratio and annealing time. We have studied the properties from the point of view that the drawing under different conditions will give different mobilities to the segments in the amorphous phase.

## 2. EXPERIMENTAL

### 2.1. Materials

The whole polymer of Avisun-1021 ($[\eta]=2.94$) and the fractions from Avisun-1021 and Toray-147 ($[\eta]=3.90$) were used for the work.

### 2.2. Fractionation

The fractionation was conducted by a column method similar to the one used by Wijga[8]. As a solvent and nonsolvent, kerosine and butyl cellosolve containing 0.5% of 2, 6-di-tertiary-butyl-para-cresol as a stabilizer were used. A 1-2% kerosin solution of the samples was mixed with sea-sand (about 60 mesh) at 135°C and precipitated by cooling the hot mixture to room temperature. The cold mixture was brought into the column and then replaced by the nonsolvent. Two methods were used for the fractionation; one was a gradient elution method at 150°C, the another, an increasing temperature method with a solvent-nonsolvent system.

### 2.3. Molecular Weight

The molecular weight of samples was determined by measuring intrinsic viscosity number in decalin at 135°C. The viscosity average molecular weight was calculated using the relation, $[\eta]=1.10\times10^{-4}M^{0.80}$, established by Kinsinger[9].

### 2.4. Density and Crystallinity

Density at 30°C was measured in a density gradient column composed of ethylene glycol and n-propylalcohol. The crystallinity of specimens was calculated from the density according to the relation:

$$\text{Crystallinity}=\frac{0.983+9(t+180)\times10^{-4}-1/d}{4.8(t+180)\times10^{-4}},$$

established by Natta[10] which was under the assumption of the additivities of the specific volumes of the crystalline and amorphous phases.

### 2.5. Preparation of Samples

Fractions, or whole polymer were molded to a film at 190°C and then quenched into ice-water. The annealed specimens were obtained from the molded films by heating them at 130°C for 3 hours between two glass plates.

### 2.6. Drawing of the Films

For the drawing experiments the quenched film (from the melt into ice water) was prepared from the whole polymer of Avisun-1021. The density and intrinsic viscosity number of the film were 0.890 g/cc and 2.94 dl/g, respectively. The specimen of the dimension of 20 mm.×15 mm.×0.4-0-5 mm. (lengthe×width ×thickness) was drawn at 25, 70 and 115°C to various lengths. The drawing at 25°C and at the other temperatures, was carried out in a water bath and in a bath of polyethylene glycol respectively, and the rate of drawing was 1 mm/sec. After the drawing, the samples was annealed at 130°C in a stretched state to avoid shrinkage during the measurement for the mechanical properties.

### 2.7. Dichroic Ratio

We measured the dichroic ratio of the drawn specimens with an IR-spectrometric instrument of Hitachi EPI-S2 type. The absorption bands at 970 $cm^{-1}$ and 995 $cm^{-1}$ which show paralell dichroic ratios were used as a parameter indicative of the orientation of the molecules. The absorptions at 970 $cm^{-1}$ and 995 $cm^{-1}$ were assingned by Liang[11], Tobin[12] and others as a wagging of methyl group and as a crystallinity sensitive band, respectively.

### 2.8. Dynamic Meachanical Properties

The temperature dependency of the dynamic modulus $E'$ and the loss tangent $\tan\delta$ for specimens was measured within the temperature range from −50°C to 100°C by a vibrating reed method, developed by Ren and Okada[7] in our laboratory. Frequency used for the measurement was approximately 100 cps. (100± 20 cps.) and the values of $E'$ and $\tan\delta$ were calculated by the following formlae given by Horio and Onogi[14].

$$E' = \frac{4\pi^2 l^4 \rho}{a_0^4 k^2}\left[\nu_r^2 + \frac{1}{8}(\Delta\nu)^2\right]$$

$$E'' = \frac{4\pi^2 l^4 \rho}{a_0^4 k^2} \cdot \nu_r \cdot \Delta\nu$$

$$\tan\delta \equiv E''/E' \cong \Delta\nu/\nu_r,$$

where $l$ and $\rho$ represent the length and density of a specimen, $\nu_r$ and $\Delta\nu$, resonance frequency and band width, respectively, and $a_0$ is a constant for the fundamental vibration whose value is 1.875 and $k^2$ the ratio of I to A, (I/A), where I and A are the moment of inertia and the area of the cross section of the specimen, respectively. The dimension of samples was ranged in (15-30 mm.)×4 mm.×(0.1-0.2 mm.) in length×width×thickness.

## 3. RESULTS AND DISCUSSION

### 3.1. Fractionation

As was described in the last section, we applied two different methods to fractionate the polymer samples, that is a gradient elution at 150°C and an increasing temperature technique with a fixed component mixture of solvent and nonsolvent. The representable results of these two methods are shown in Fig. 1 and Fig. 2.

Table 1. Increasing temperature fractionation. (Fractionation A)

| Fraction No. | Temperature (°C) | Extracted weight (gr.) | Extract w% | Cumulative w% | $[\eta]$ (100 ml/gr.) | $\bar{M}_v$ ($\times 10^5$) | Density (at 30°C) |
|---|---|---|---|---|---|---|---|
| A- 1 | 30~ 70 | 0.603 | 2.668 | 1.334 | 2.18 | 2.35 | 0.872 |
| A- 2 | 70~ 80 | 0.510 | 2.257 | 3.796 | 0.70 | 0.60 | 0.882 |
| A- 3 | 80~ 90 | 0.982 | 4.343 | 7.096 | 0.93 | 0.83 | 0.892 |
| A- 4 | 90~100 | 2.054 | 9.081 | 13.808 | 0.83 | 0.70 | 0.902 |
| A- 5 | 100~111 | 1.820 | 8.048 | 22.373 | 1.33 | 1.21 | 0.906 |
| A- 6 | 111~116 | 1.184 | 5.237 | 29.016 | 1.49 | 1.47 | 0.906 |
| A- 7 | 116~121 | 1.755 | 7.761 | 35.515 | 1.88 | 1.97 | 0.906 |
| A- 8 | 121~123 | 0.605 | 2.677 | 40.734 | 2.28 | 2.47 | 0.909 |
| A- 9 | 123~125 | 0.567 | 2.507 | 43.326 | 2.78 | 3.15 | 0.908 |
| A-10 | 125~150 | 12.532 | 55.419 | 72.289 | 4.60 | 5.40 | 0.909 |

Table 2. Gradient elution fractionation. (Fractionation B)

| Fraction No. | Conc. of kerosine (%w) | Extracted weight (gr.) | Extract w% | Cumulative w% | $[\eta]$ (100 ml/gr.) | $\bar{M}_v$ ($\times 10^5$) | Density (at 30°C) |
|---|---|---|---|---|---|---|---|
| B-1 | 3 | 2.246 | 21.15 | 10.58 | 0.90 | 0.80 | 0.903 |
| B-2 | 6 | 2.248 | 21.16 | 31.73 | 2.27 | 2.45 | 0.906 |
| B-3 | 15 | 2.209 | 20.30 | 52.46 | 3.03 | 3.50 | 0.909 |
| B-4 | 18 | 0.183 | 1.72 | 63.47 | 4.37 | 5.52 | — |
| B-5 | 24 | 2.568 | 24.18 | 76.32 | 4.35 | 5.49 | 0.911 |
| B-6 | 27 | 0.193 | 1.82 | 89.32 | — | — | — |
| B-7 | 33 | 0.455 | 4.28 | 92.37 | 4.57 | 5.85 | 0.918 |
| B-8 | 36 | 0.305 | 2.87 | 95.95 | 4.59 | 5.87 | 0.918 |
| B-9 | 100 | 0.215 | 2.02 | 98.39 | 4.90 | 6.40 | — |

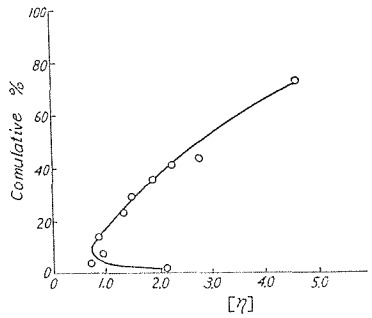



Fig. 1. Integral distribution curve for the fractionation by the increasing temperature method.

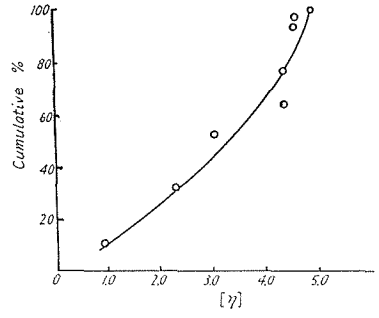



Fig. 2. Integral distribution curve for the fractionation by the gradient elution method.

It is reported by Wijga and his coworker[8] that the increasing temperature method with a given solvent separates the polypropylene sample according to crystallinity, while the gradient elution method at a chosen temperature sufficiently near the melting point of the sample fractionates it according to molecular weight. We have also obtained similar results to theirs. Intrinsic viscosity-density relationship of the obtained fractions is shown in Fig. 3, comparing

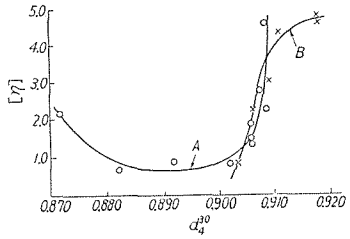



Fig. 3. Intrinsic viscosity number *vs.* density of polypropylene fractions.
Curve A : Increasing temperature method
Curve B : Gradient elution method

Table 3. Dynamic mechanical properties of polypropylene fractions.

| Fraction No. | [η] (100 ml/gr.) | Density at 30°C | Crystallinity (%) | $T_a$(°C) | E′-30 ($10^{10}$ dyne/cm²) | tan δ at $T_a$ ($\times 10^{-2}$) |
|---|---|---|---|---|---|---|
| A- 2 | 0.70 | 0.882 | 37.8 | −2 | 0.82 | ⩾10.2 |
| A- 3 | 0.93 | 0.892 | 50.4 | 12 | 3.58 | 7.78 |
| C- 2 | 0.73 | 0.895 | 54.2 | 19 | 2.35 | 7.10 |
| D- 1 | 0.84 | 0.898 | 57.8 | 13 | 3.64 | 6.34 |
| A- 4 | 0.83 | 0.902 | 62.7 | 14 | 3.66 | 4.81 |
| B- 1 | 0.90 | 0.903 | 63.9 | 14 | 4.46 | 4.58 |
| C- 3 | 1.68 | 0.902 | 62.7 | 19 | 2.80 | 5.48 |
| F- 1 | 1.51 | 0.903 | 63.9 | 14 | 4.25 | 4.50 |
| E- 1 | 1.61 | 0.904 | 65.1 | 14 | 3.58 | 4.99 |
| D- 2 | 1.76 | 0.905 | 66.4 | 16 | 3.44 | 5.33 |
| A- 7 | 1.88 | 0.906 | 67.6 | 15 | 2.69 | 5.38 |
| F- 3 | 2.21 | 0.906 | 67.6 | 16 | 4.82 | 4.27 |
| B- 2 | 2.27 | 0.906 | 67.6 | 13 | 3.41 | 4.41 |
| D- 3 | 2.62 | 0.906 | 67.6 | 15 | 3.47 | 4.37 |
| C- 5 | 2.82 | 0.906 | 67.6 | 18 | 2.75 | 4.32 |
| C- 3 | 1.68 | 0.902 | 62.7 | 19 | 2.80 | 5.48 |
| F- 1 | 1.51 | 0.903 | 63.9 | 14 | 4.25 | 4.50 |
| E- 1 | 1.61 | 0.904 | 65.1 | 14 | 3.58 | 4.99 |
| D- 2 | 1.76 | 0.905 | 66.4 | 16 | 3.44 | 5.33 |
| A- 7 | 1.88 | 0.906 | 67.6 | 15 | 2.69 | 5.38 |
| F- 3 | 2.21 | 0.906 | 67.6 | 16 | 4.82 | 4.27 |
| B- 2 | 2.27 | 0.906 | 67.6 | 13 | 3.41 | 4.41 |
| D- 3 | 2.62 | 0.906 | 67.6 | 15 | 3.47 | 4.37 |
| C- 5 | 2.82 | 0.906 | 67.6 | 18 | 2.75 | 4.32 |
| A- 9 | 2.78 | 0.908 | 70.4 | 14 | 3.52 | 4.38 |
| E- 2 | 2.20 | 0.916 | 79.5 | 15 | 4.50 | 3.86 |
| F- 4 | 2.74 | 0.919 | 80.8 | 24 | — | 3.25 |
| E- 3 | 3.43 | 0.909 | 71.2 | 14 | 3.39 | 4.49 |
| D- 4 | 3.57 | 0.914 | 77.2 | 13 | 4.34 | 4.15 |
| D- 5 | 3.87 | 0.916 | 79.5 | 17 | 2.84 | 3.90 |
| B- 7 | 4.59 | 0.906 | 67.6 | 13 | 4.19 | 4.45 |
| E- 4 | 4.82 | 0.906 | 67.6 | 14 | 3.80 | 4.30 |
| A-10 | 4.60 | 0.909 | 71.2 | 14 | 4.85 | 3.84 |
| C- 8 | 4.80 | 0.911 | 73.6 | 17 | 3.07 | 3.90 |

the results by the two methods. It is obvious from Fig. 3 that the fractionation by the increasing temperature method occurs widely in accordance with crystallinity.

### 3.2. Dynamic Mechanical Properties of the Fractions

In Table 3, the dynamic modulus $E'$, maximum value of $\tan\delta$ and temperature $T_a$, where $\tan\delta$ value goes through a maximum, are shown together with some other physical properties. In the table the fractions having nearly molecular weights are shown as a family in order to compare the results at a same level of molecular weight. Temperature-$\tan\delta$ curves for the fractions with relatively smaller molecular weights and relatively lower crystallinities are shown in Fig. 4 and those for the other fractions are shown in Fig. 5. As is shown in Fig. 4, $T_a$ shifts to a higher temperature with the increase of the crystallinity, but such small difference in the crystallinity as between sample A-3, D-1 and B-1 does not appreciably change $T_a$-position.

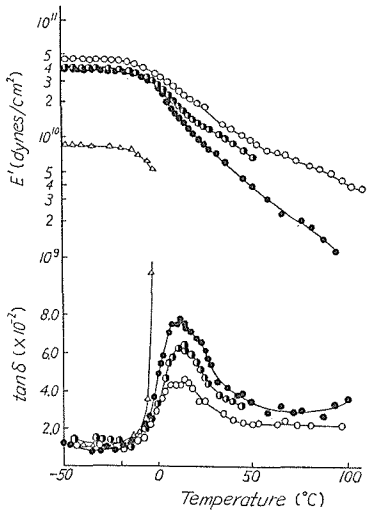



Fig. 4. Dynamic modulus and loss tangent *vs.* temperature for polypropylene fractions.
△: sample A-2, $[\eta]=0.70$, C=37.8%
●: sample A-3, $[\eta]=0.93$, C=50.4%
◑: sample D-1, $[\eta]=0.84$, C=57.8%
○: sample B-1, $[\eta]=0.90$, C=63.9%
C: Crystallinity %

In accordance with the increase of the crystallinity, the height of the peak of $\tan\delta$ in the $\alpha_a$-absorption considerably diminishes and the dynamic molulus $E'$ becomes higher, whereas the temperature range, where $E'$ diminishes rapidly, well corresponds with that of the $\alpha_a$-absorption in the $\tan\delta$ curve and the diminuation is more rapid for a low crystallinity sample. These tendencies in $\tan\delta$ and $E'$ curves are in good accordance with the other's results obtained for crystalline polymers. Although it is generally believed that the width of the absorption should become broader with increasing of the crystallinity, however, as shown in our data for low molecular weight fractions, the broaden-

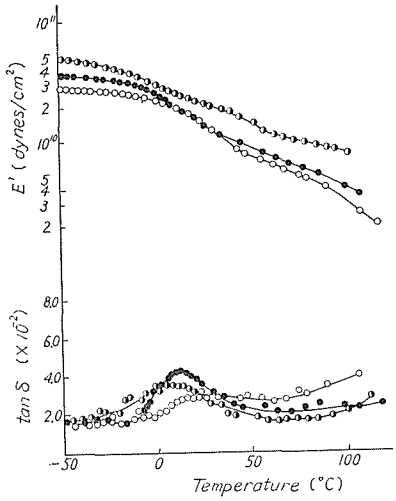



Fig. 5. Dynamic modulus and loss tangent *vs.* temperature for polypropylene fractions.
●: sample B-2, $[\eta]=2.27$, C=67.6%
◑: sample E-2, $[\eta]=2.20$, C=79.5%
○: sample F-4, $[\eta]=2.74$, C=80.8%
C : Crystallinity %

ing of the absorption does not occur appreciably. On the other hand, in the case of the higher molecular weight and crystallinity, the broadening of the absorption width is observed apparently as had been expected (see Fig. 5).

We may interpret these results in terms of molecular mobility. It is generally recognized that the absorption in the vicinity of room temperature is due to the micro Brownian motion of the main chain segments in the amorphous phase of polypropylene. Hence it may be assumed that a $\tan\delta$ value at a temperature corresponds to the amounts of the segments whose relaxation times at the temperature are of the order of the time scale of the measurement. The position of $T_a$ by the measurement at constant frequency may be affected by the magnitude of a restriction to segmental motions given by the crystallites and other structual factors. Furthermore, the width of the absorption may depend on the heterogeneity of the magnitude of the restriction caused from the variety of the fine structure. Thus, it is predicted that the weight fraction of the amorphous phase of specimens is proportional to the area of the $\alpha_a$-absorption. Under these assumptions we will now attempt to explain the experimental results.

For the fractions shown in Fig. 4, the area between the temperature axis and the curve of $\tan\delta$ in $\alpha_a$-absorption range decreases with increasing of the crystallinity. This indicates that the crystallinity is inversely proportional to the area. The shifting of $T_a$ to a higher temperature with increasing of the crystallinity may suggest that the motion of the segments in the amorphous phase is restricted by the crystallites which coexist with the amorphous segments in the polymer structure. But for the fractions whose molecular weight and crystallinity are relatively low, the mobility of the segments will not be so much re-

stricted as in the case of a sample of high crystallinity, particularly after a sufficient annealing at 130°C. Consequently, it would be reasonably explained that $T_\alpha$ did not appreciably depend on the crystallinity except for the sample A-2, and the widths of the $\alpha_a$-absorption for the three fractions became nearly equal, since the variety of the fine structure related to the extent of the mobility of the segments in the amorphous phase was probably not so distinguishable.

In the case of Fig. 5, because of the high crystallinity and high molecular weight, the fine structure of the samples will be much complicated and therefore will be a wide variety of the restrictions to the mobility of the chain segments in the amorphous phase. Moreover, the higher the crystallinity, the variety of the restriction will be the wider, while the degree of the restriction will increase with increaing of the crystallinity. Thus as is shown in Fig. 5, $T_\alpha$ or $\alpha_a$-absorption band shifts to a higher temperature and the width of the absorption becomes wider with increasing crystallinity.

It is ascertained from the data that the maximum value of $\tan\delta$ is proportional to the area $S$, $S=\int_{-30}^{50} f(T)\cdot dT$ where $f(T)=\tan\delta$, and $T$ is temperature (°C). Hence, we plotted in Fig. 6 the maximum value of $\tan\delta$ against crystallinity for all fractions examined herein. It seems that there is an inflexion point in the vicinity of 60-70% of the crystallinity and this fact may mean that the fine structure becomes more complex if the crystallinity exceeds 60-70%. The experimental point, open circle in Fig. 6 shows the result for the unfractionated whole polymer quenched into ice-water from the melt, where the apparent crystallinity of this sample was also calculated from the density.

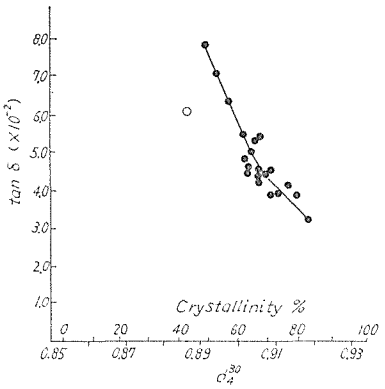



Fig. 6. Relation between maximum value of $\tan\delta$ and crystallinity of polypropylene fractions.
○ : data for whole polymer quenched into ice-water from melt.

If the area instead of the maximum value of $\tan\delta$ were plotted against crystallinity, all experimental points for the fractions and the quenched polymer might comprise a unique curve without exception as could be supposed from the data in Fig. 7. However, the extreme heterogeneity of the fine structure in the quenched state may be implicit from the fact that there is apparent difference in the maximum value of $\tan\delta$ between for the quenched whole polymer and for the annealed fraction of the same crystallinity.

### 3.3. Dynamic Mechanical Properties of Quenched Polypropylene

Another evidence to support the above mentioned concept is the result for a series of samples of different thermal histories. In Fig. 7, $E'$ and $\tan\delta$ *vs.* temperature are shown for the sample which have been quenched from melt into dryice-methanol, ice-water and annealed after the quenching or cooled slowly from melt.

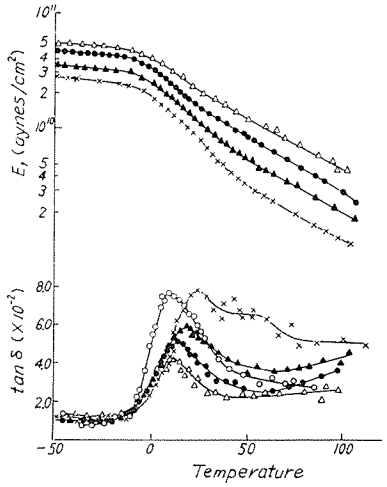



Fig. 7. Dynamic modulus and loss tangent *vs.* temperature for whole polymer of polypropylene quenched into dry ice-methanol (×), quenched into ice-water (▲) from melt, annealed at 130°C for 3 hrs after the quenching into ice-water (●), cooled slowly from melt (△) and fraction A-3 (○) whose density is nearly equal to that of sample quenched into ice-water.
×: $[\eta]=2.94$, $d_4^{30}=0.885$ ▲: $[\eta]=2.94$, $d_4^{30}=0.890$ ●: $[\eta]=2.94$, $d_4^{30}=0.903$
○: $[\eta]=0.93$, $d_4^{30}=0.892$ △: $[\eta]=2.94$, $d_4^{30}=0.914$

Temperature $T_\alpha$ of quenched samples is higher than that of the annealed or slowly cooled one, while the densities are lower than the latter ones. And the lower the quenched temperature is, the higher the $T_\alpha$ is.

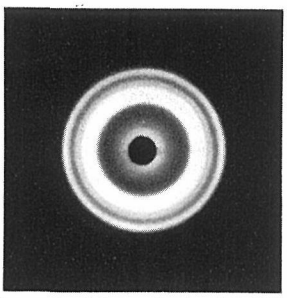
On the other hand, $T_\alpha$ for the slowly cooled one is lower than for the annealed one, though the crystallinity of the former is higher than the latter and in recent study in our laboratory it is found that the $T_\alpha$ of an annealed polypropylene approaches that of an isothermally crystallized one at a high temperature sufficiently near the melting point of the polymer and slowly cooled to room temperature, with increasing of the annealing temperature.

In addition the width of the absorption is wider for the quenched sample and the maximum value of $\tan\delta$ is larger than for the annealed or slowly cooled ones. The difference in the viscoelastic behavior between well annealed fraction A-3 and quenched sample (into ice-water) of the same density can be apparently observed. This means that the temperature $T_\alpha$ and the width of the $\alpha_a$-absorption for a crystalline polymer like polypropylene do not change only by difference in the crystallinity, but can change by difference in its thermal history.

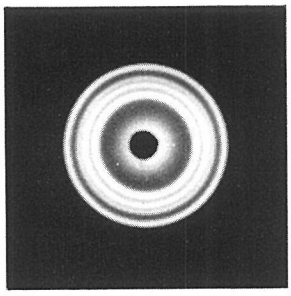
The differences in viscoelastic behavior will correspond to the difference in the mobility of segments in the amorphous phase of samples due to the difference in the fine structures[15~18]. In other words, in quenched sample there may exist a paracrystalline structure having small crystalline size and also there may remain some amount of internal stress which affects the mobility of the segments. Hence the fine structure of the quenched one may be more complicated than the annealed ones. By the annealing of the quenched sample the paracrystalline structure will be converted to a more perfect crystalline structure and the internal stress having remained will be relaxed and as a result of the annealing the restriction to the movement of segments decreases and will be more simplified. By this reason $T_\alpha$ shifts to a lower temperature and the width of the absorption becomes narrower with annealing and increasing of the annealing temperature.

When sample have been cooled slowly from melt, the crystalline structure may be more perfect and simple, and the internal stress having remained may be more small than when annealed. As shown in Fig. 7, $T_\alpha$ is lower and the width is narrower for the slowly cooled sample than the annealed one.

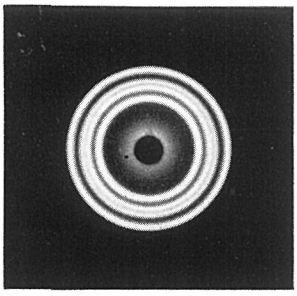
In order to get an information of the crystallization process during the quenching and annealing of samples, we have obtained the X-ray diffraction patterns of the samples having different thermal histories (Fig. 8). In the pattern for specimen quenched into dryice-methanol, the diffractions from the plane (110) and (040) are not clear and the other result for this polymer by a diffractometer shows that there appear only two clear peaks of the diffraction at $2\theta=15°$ and 22°. The results indicate that there exists the paracrystalline struc-



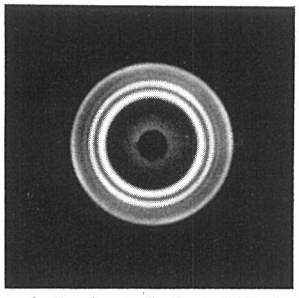
Quenched into dryice-MeOH



Quenched into ice-water



Annealed at 130°C for 3 hrs.



Fraction A-3 Annealed at 130° for 3 hrs.

Fig. 8. X-ray differaction pattern of quenched, annealed whole polymer of polypropylene and fraction A-3.

ture in this quenched polypropylene.

When quenched sample is annealed, the diffraction pattern changes to the one as shown in the Figure. But Wyckoff[17] reported that even after annealing of polypropylene at 130°C there remained some amounts of paracrystalline structure and by annealing at 70°C and 160°C the lateral dimension of the crystallites changed from 50Å to 200Å. He concluded from these results that there occurred a recrystallization by annealing at a temperature above 130°C. Therefore we can suppose that, when the quenched sample is annealed at a higher temperature than 130°C, $T_a$ may shift to a lower temperature than the $T_a$ for the one annealed at 130°C. In fact, the other result to support of above consideration has been obtained in our recent study, that is, in the experiments by another type of instrument we have observed that the $T_a$ (in the curve of $E''$ against temperature) of the sample annealed at 150°C is 3°C lower than that of the one annealed at 135°C.

We can consider that the shape of the $\tan\delta$ curve and the temperature $T_a$ are also related to the paracrystalline structure, the size of the crystallite and the internal stress having remained, because these factors are related to the degree of the restriction to the mobility of the segments and to the distribution of the force of the restriction.

From the point of view that the fine structure of a quenched sample is more complex than the structure of annealed one and of the slowly cooled sample from the melt is more simple than the annealed one, we have plotted $T_a$ against density of these samples in Fig. 9. In this case we can take the density as a measure indicative of the heterogeneity of the fine structure.

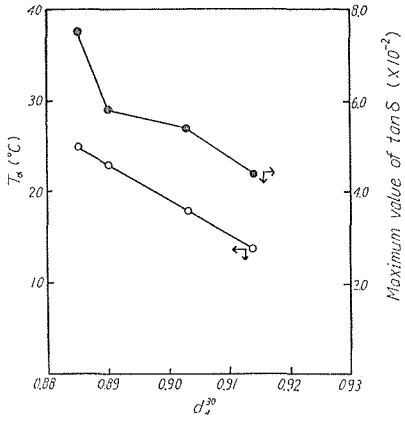



Fig. 9. Transition temperature ($T_a$) and maximum value of $\tan\delta$ *vs.* density of quenched, annealed and slowly cooled polypropylene.
○: $T_a$ ●: maximum value of $\tan\delta$

As we have pointed out, the shape of $\tan\delta$ curve, maximum value of $\tan\delta$ and temperature $T_a$ depend not only on the crystallinity of the sample but also strongly depend on its thermal history which brings about a difference in the fine structure. Therefore, when we attempt to examine the viscoelastic behavior of polypropylene or other crystalline polymers, we must take the thermal

Table 5. Dichroric ratio of drawn polypropylenene films at 970 cm and 970 cm.

| Drawing temperature (°C) | Draw ratio | Annealing time (min.) | Dichroric ratio | |
|---|---|---|---|---|
| | | | at 970 $cm^{-1}$ | at 995 $cm^{-1}$ |
| 25 | 7.0 | 5.0 | 6.20 | 36.98 |
| 〃 | 〃 | 10.0 | 5.30 | 19.73 |
| 〃 | 〃 | 30.0 | 5.64 | 18.27 |
| 〃 | 〃 | 60.0 | 5.75 | 22.63 |
| 〃 | 〃 | 120.0 | 5.41 | 21.53 |
| 70 | 7.0 | 5.0 | 6.37 | 23.23 |
| 〃 | 〃 | 10.0 | 5.90 | 19.99 |
| 〃 | 〃 | 20.0 | 5.66 | 18.65 |
| 〃 | 〃 | 30.0 | 5.86 | 19.95 |
| 〃 | 〃 | 60.0 | 5.16 | 17.52 |
| 〃 | 〃 | 120.0 | 5.61 | 18.70 |
| 115 | 7.0 | 10.0 | 4.04 | 12.23 |
| 〃 | 8.5 | 〃 | 4.06 | 14.33 |
| 〃 | 10.5 | 〃 | 4.50 | 14.35 |
| 〃 | 14.0 | 〃 | 6.29 | 23.68 |

Table 4. Dynamic mechanical properties of drawn polypropylene films.

| Drawing temperature (°C) | Draw ratio | Annealing time (min) | Density at 30°C (gr/cc) | E′ at−30°C ($\times 10^{10}$ dyne/$cm^2$) | $T_d$ (°C) | tan $\delta$ at $T_d$ ($\times 10^{-2}$) |
|---|---|---|---|---|---|---|
| 25 | 7.0 | 10 | 0.898 | 8.00 | 28 | 5.20 |
| 〃 | 〃 | 120 | 0.904 | 9.30 | 23 | 6.10 |
| 〃 | 10.5 | 10* | 0.895 | 6.75 | 28 | 3.85 |
| 〃 | 〃 | 120* | 0.897 | 11.80 | 23 | 4.75 |
| 70 | 7.0 | 10 | 0.903 | 10.90 | 21 | 4.20 |
| 〃 | 〃 | 120 | 0.905 | 9.90 | 22 | 4.90 |
| 〃 | 10.5 | 10* | 0.902 | 13.00 | (35) | 3.65 |
| 〃 | 〃 | 120 | 0.905 | 11.45 | 28 | 4.20 |
| 115 | 7.0 | 10 | 0.902 | 10.00 | 19 | 5.20 |
| 〃 | 〃 | 60 | 0.903 | 12.20 | 18 | 5.25 |
| 〃 | 10.5 | 10 | 0.901 | 12.10 | 20 | 4.00 |
| 〃 | 〃 | 60 | 0.902 | 12.20 | 25 | 4.15 |
| 〃 | 14.0 | 10* | 0.892 | 14.40 | 26 | 2.80 |
| 〃 | 〃 | 60 | 0.902 | 12.35 | 25 | 3.15 |
| 115 | 7.0[a] | 10 | 0.902 | 9.95 | 18 | 4.20 |
| 〃 | 10.5[a] | 〃 | 0.901 | 13.00 | (35) | 2.60 |
| 〃 | 14.0[a] | 〃* | 0.892 | 14.50 | (35) | 2.50 |

1) Molded films quenched from melt were drawn to indicated rations before or after the annealing at 130°C for 2 hours, and after the annealing they were annealed at 130°C for indicated periods of time under fixed length.
Samples marked (a) were drawn after annealing and the others were before annealing.
2) Samples marked (*) were cloudy.
3) Data in ( ) indicate that the samples did not show clear peaks in the tan $\delta$ curves.

history of a sample in mind, particularly when we examine the temperature $T_a$ and the crystallinity dependency of the viscoelastic properties.

### 3.4. Dynamic Mechanical Properties of Drawn Polypropylene Films

The mobility of the segments in the amorphous phase of a crystalline polymer is thought to depend greatly on the orientation of the molecular chains. Therefore, we study in this section an influence of the drawing of polypropylene film under various conditions on its viscoelastic behaviors.

The molded film of the whole polymer was drawn under different conditions, as described in the experimental section and the dynamic mechanical properties and the dichroric ratios of the drawn films were studied. All the data are summarized in Tables 4 and 5.

**3.4.1. The effect of drawing temperature.** The molded films were drawn to given lengths at 25°C, 70°C and 115°C and annealed at 130°C for 10 min. in order to prevent the shrinkage of the specimens during the measurement of the temperature dependency of the dynamic mechanical properties (see section 2-6).

By the drawing of 7 times, $T_a$ shifts to a higher temperature as the drawing temperature decreases in a comparison with that of the undrawn sample and the maximum value of $\tan\delta$ and the area under the absorption curve are minimum when the sample is drawn at 70°C. Almost similar tendency was observed also when it was drawn up to 10.5 times. However, in this case, $\tan\delta$ curve did not show distinct peak, though the value of $\tan\delta$ was minimum when the sample was drawn at 70°C.

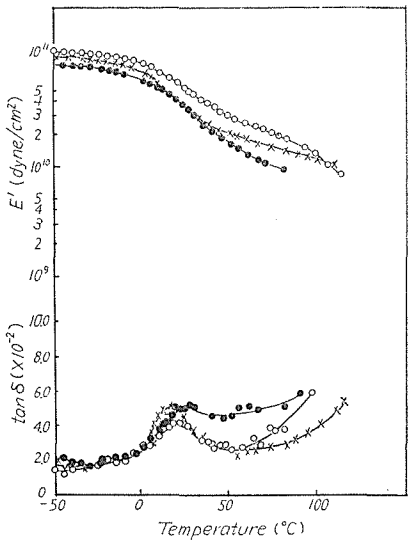



Fig. 10. Dynamic modulus and loss tangent *vs.* temperature of polypropylene film drawn at 25°C ●, 70°C ○, and 115°C ×. The films were annealed at 130° for 10 min. after the drawing. The draw ratio was 7.0.

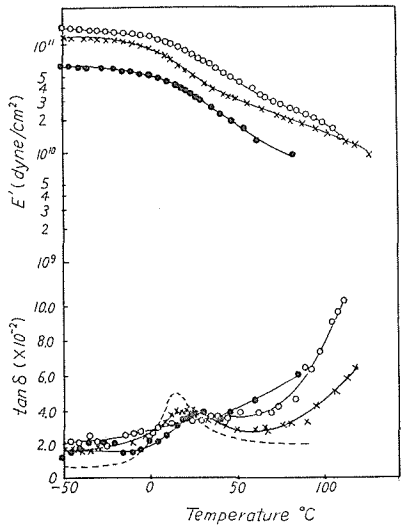



Fig. 11. Dynamic modulus and loss tangent *vs.* temperature of polypropylene film drawn at 25°C ●, 70°C and 115°C ×. The films were annealed at 130°C for 10 min. after the drawing. The draw ratio was 10.5. (·····) is the data for undrawn polypropylene film which was annealed at 130°C for 2 hrs (the density at 30°C was 0.903).

Tan $\delta$ curves for the samples drawn at 25°C resemble those for the undrawn quenched samples which has been shown in the previous section in their shape regardless of the degree of the drawing. This resemblance seems to indicate that there exists in the cold drawn films the paracrystalline structure which was observed by Wyckoff[17] for a cold drawn polypropylene. On the other hand, the dynamic modulus $E'$ is highest for the sample drawn at 70°C and decreases in the order of the drawn temperature 115°C and 25°C. As is shown in Table 5, the film drawn at 70°C has the largest value of the dichroic ratio and the density equal to that of the film drawn at 115°C but greater than that of the film drawn at 25°C. The result that the film shows the largest value of the dynamic modulus and the smallest value of maximum tan $\delta$ when it is drawn at 70°C, may be explained in terms of the highest degree of orientation of this film.

In the tan $\delta$ curves in Fig. 10 and Fig. 11 it is shown that the widths of the absorption for drawn samples are wider than for the undrawn sample. These results may be interpreted also in terms of the molecular motion. The mobility of the segments in the amorphous phase in drawn film may be restricted more strongly than in undrawn one and the distribution of the degree of the restriction may be broader than in undrawn film. If one interprets these consideration collectively, temperature range of $\alpha_a$-absorption is thought to shift to a lower temperature, as the result that a fraction of the segments whose relaxation times are of the order of the time scale of the measurement in the temperature range of $\alpha_a$-absorption increases as the drawing temperature elevates. Furthermore, it could be also supposed that the drawing at higher temperatures was being done accompanying with the relaxation of the internal stress, so that the restriction to the segment was decreased.

On the other hand, the segments in the amorphous phase whose mobility has been restricted by the drawing are thought not to move unless the temperature elevates. This consideration may be in good accordance with the fact that the absorption observed in the vicinity of 120°C is largest for the sample which has been drawn at 70°C and has the smallest $\alpha_a$-absorption, where some onset of mobility of the molecular chains in the crystalline phase is reported to occur in the vicinity of 120°C[5]. Here, if any mobility is given to the chains in the crystalline phase, there may occur some possibility to the reorientation and recrystallization of the molecules. This means that the absorption peak in the vicinity of 120°C is closely related with the orientation and the mobility of the segments in amorphous phase.

**3.4.2. The Effect of Draw Ratio.** $E'$ and tan $\delta$ *vs.* temperature curves for the samples which have been drawn to 7, 10.5 and 14 times at 25°C, 70°C and 115°C are shown in Figs. 12, 13 and 14 respectively. It is observed that independently of the drawing temperature $T_a$ of the drawn samples shifts to a higher temperature and the maximum value of tan $\delta$ decreases as the draw ratio increases. In relation to the absorption in the vicinity of 120°C, the degree of the absorption exhibits to increase as much as the draw ratio becomes higher, hence as the $\alpha_a$-absorption smaller. In addition the dynamic modulus $E'$ increases and

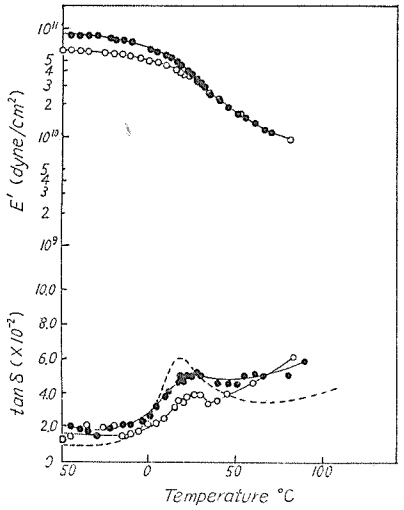



Fig. 12. Dynamic modulus and loss tangent *vs.* temperature of polypropylene film drawn at 25°C and annealed at 130°C for 10 min.
Draw ratio : 7.0 ●, 10.5 ○.
……: undrawn polypropylene film quenched from melt (the density was 0.890 at 30°C)

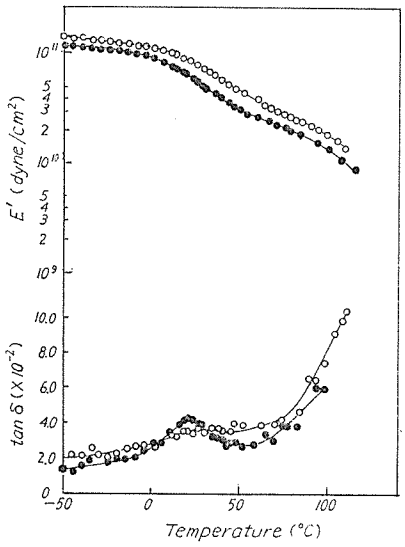



Fig. 13. Dynamic modulus and loss tangent *vs.* temperature of polypropylene film drawn at 70°C and annealed at 130°C for 10 min.
Draw ratio : 7.0 ●, 10.5 ○.

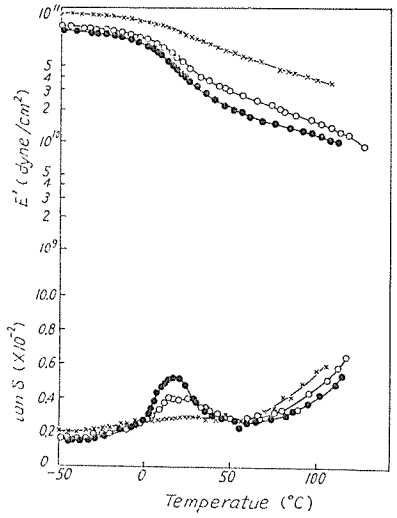



Fig. 14. Dynamic modulus and loss tangent *vs.* temperature of polypropylene film drawn at 115°C and annealed at 130°C for 10 min.
Draw ratio : 7.0 ●, 10.5 ○, 14.0 ×.

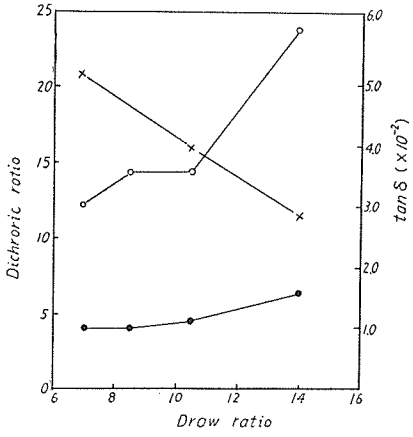



Fig. 15. The relation between draw ratio and dichroric ratio of polypropylene film drawn at 115°C and annealed at 130°C for 10 min. ; ● at 970 $cm^{-1}$ : ○ 995 $cm^{-1}$ : × maximum tan $\delta$ value.

the change of the slope of it in the temperature range of $\alpha_a$-absorption becomes less as the draw ratio increases.

On the other hand, the dichroric ratio and the maximum value of $\tan\delta$ are plotted against the draw ratio in Fig. 15, where the film was drawn to chosen ratios at 115°C and annealed at 130°C for 10 minutes and the resultant drawn films showed almost the same density. It is ascertained from the figure that the dynamic modulus $E'$ changes only accordingly to the molecular orientation, because the densities of samples are almost the same.

The fact that $T_a$ shifts to a higher temperature and the maximum value of $\tan\delta$ decreases with increasing of the draw ratio may be attributed to the increase of the internal stress having stored and hence to the increase of the degree of the restriction given to the movement of the segments in the amorphous phase, in accordance with increasing of the draw ratio. The result that the film drawn at 70°C gives the smallest maximum value of $\tan\delta$ and the highest temperature of $T_a$ as described in the last section, may also be explained by the similar reason that the internal stress stored becomes highest when the film has been drawn at the temperature 70°C.

**3.4.3. The Effect of the Annealing.** The change of the dichroric ratios of the drawn films (at 25°C and 70°C) by the anndaling at 130°C for various periods of time are shown in Fig. 16. The degree of orientation sharply decreases by the annealing for 10 min. but it seems that the dichroic ratio does ont change further appreciably by the annealing for more than 10 min. It is very interesting that the dichroic ratio in the crystallinity sensitive band 995 $cm^{-1}$ changes remarkably by the annealing. The ratios at the band are expected to represent the relative degree of the orientation of the crystalline chains, but further study

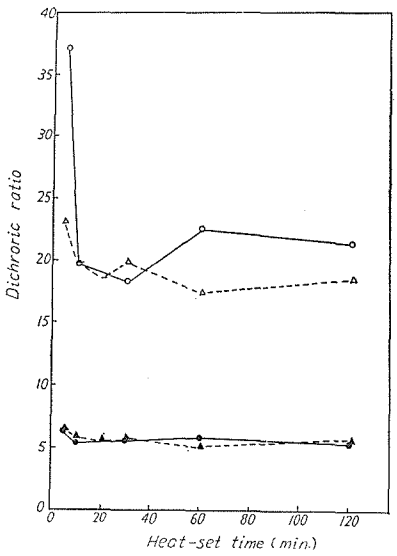



Fig. 16. The variation of dichroric ratio with annealing time. The polypropylene film was annealed after drawing to a ratio of 7.0. The films were drawn at 25°C (●, ○) and 70°C (▲, △).
●, ▲ : dichroric ratio at 970cm$^{-1}$ ○, △ : dicroric ratio at 995cm$^{-1}$

will be necessary to confirm the relations. Meanwhile, there is not observed appreciable change in the dichroic ratio by annealing of the sample, if it has been drawn at 115°C.

$E'$ and $\tan\delta$ curves for the samples drawn to 7 times at 25°C and 70°C and annealed at 130°C for 10 and 120 min. are shown in Figs. 17 and 18. In these figures it is observed that the maximum value of $\tan\delta$ of the samples annealed for 120 min. is greater than that for 10 min. and $T_\alpha$ for the former is lower than that for the latter. By the annealing of the film drawn at 115°C there is not observed noticeable difference in the $\tan\delta$ and $E'$ curves and this result well coincides with the result obtained in the study of the dichroric ratio above mentioned.

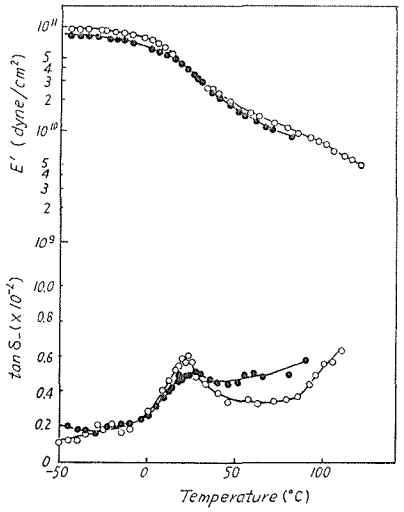



Fig. 17. Dynamic modulus and loss tangent *vs.* temperature of polypropylene film drawn at 25°C (draw ratio, 7.0) and annealed at 130°C for 10 min. ●, and 120 min. ○.

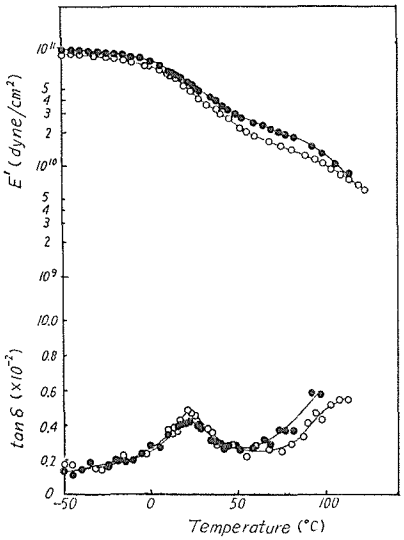



Fig. 18. Dynamic modulus and loss tangent *vs.* temperature of polypropylene film drawn at 70°C (draw ratio, 7.) and annealed at 130°C for 10 min. ●, and 120 min. ○.

The densities of the films are greater for the samples annealed for 120 min. in both cases. The reason why the samples annealed for 120 min. show greater values of maximum $\tan\delta$ and a lower value of $T_\alpha$ though their crystallinities are greater than for the samples annealed for 10 min. may be that the restriction to the mobility of the segments in the amorphous phase is weakened as a result of the relaxation of the internal stress which can occur simultaneously with the recrystallization.

**3.4.4. The Effect of the Thermal History of Samples before Drawing.** The thermal history of samples is thought to impart great influence on the effect of drawing. The quenched samples from melt were drawn to chosen ratios at different temperatures before and after annealing at 130°C for 2 hours. The value of $T_\alpha$ and $\tan\delta$ at $T_\alpha$ are much affected by the fact that whether the annealing was carried out before drawing or not as shown in Table 4. For example, the

drawn smples annealed before drawing do not exhibit clear peaks in the tan $\delta$ curve (samples without clear peak are enclosed in brackets in the taable), while the drawn samples without pre-annealing indicate clear peaks in the tan $\delta$ curve. For drawn samples without pre-annealing, $T_a$ shifts to a higher temperature and tan $\delta$ at $T_a$ decreases as the degree of drawing increases from 7.0 to 10.5 and 14.0 times, while for drawn samples with pre-annealing the tendencies seem to appear only in the lower range of the degree of drawing so that $T_a$ shifts to a higher temperature and tan $\delta$ decreases as the degree of drawing increases from 7.0 to 10.5 times but there exhibits no further change from 10.5 to 14.0 times.

In Fig. 19 is made a comparison of the tan $\delta$ curve between drawn two samples: one of the samples was annealed and the other was not annealed before drawing both to 7 times at 115°C. Tan $\delta$ at $T_a$ is lower for the former than for the latter but $T_a$ is almost same for both samples, where the density at room temperature and dynamic modulus, $E'$ at below the temperature of $T_a$ are equivalent.

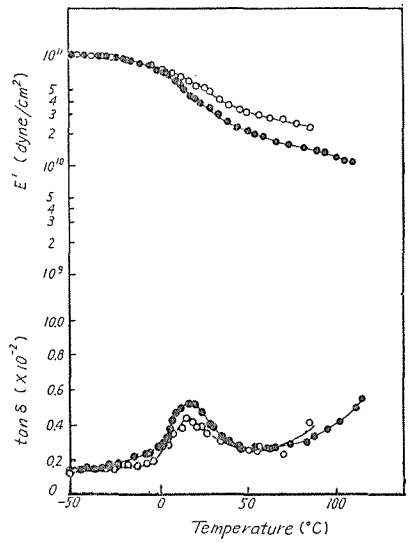



Fig. 19. Dynamic modulus and loss tangent *vs.* temperature of polypropylene film annealed at 130°C for 10 min. after drawing at 115°C to the ratio of 7.0.
● : drawn before annealing. ○ : drawn after annealing.

From these results it can be supposed that when annealed film is drawn there will be stored a greater amount of internal stress in the polymer segments than for the case of drawing of quenched film which is more amorphous than the annealed one. Therefore in the case of drawing of the annealed film, the amount of the segments which is restricted to move may be greater and also the degree of the restriction may be stronger than in the case of drawing of the quenched film.

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